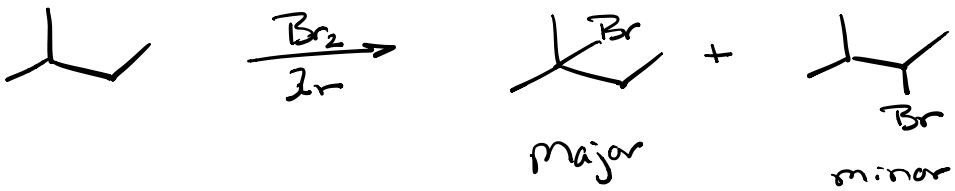
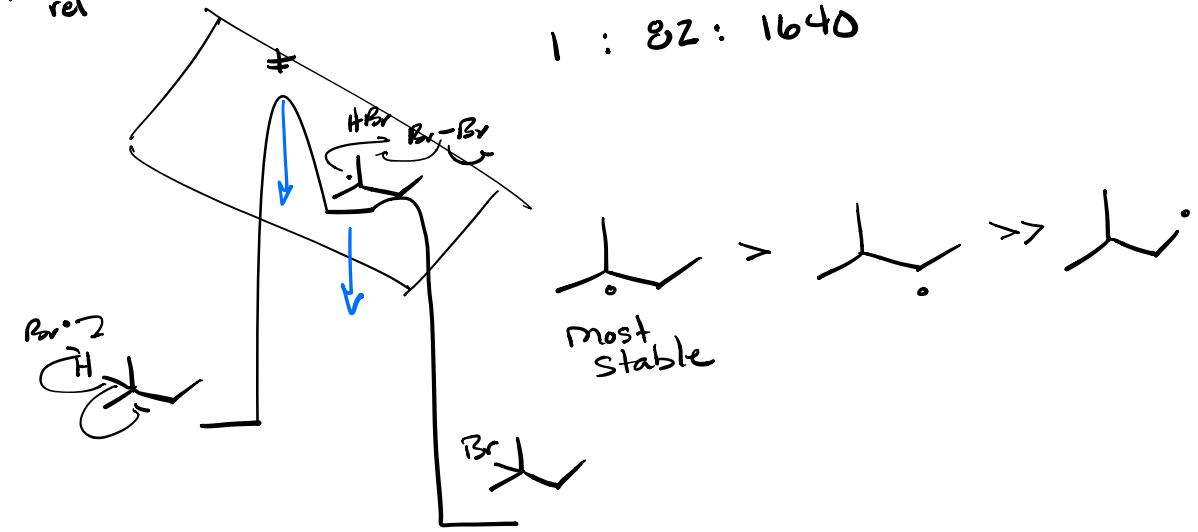
Free Radical Reactions

Regioselectivity

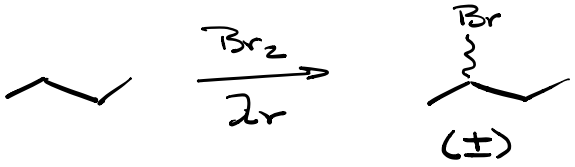


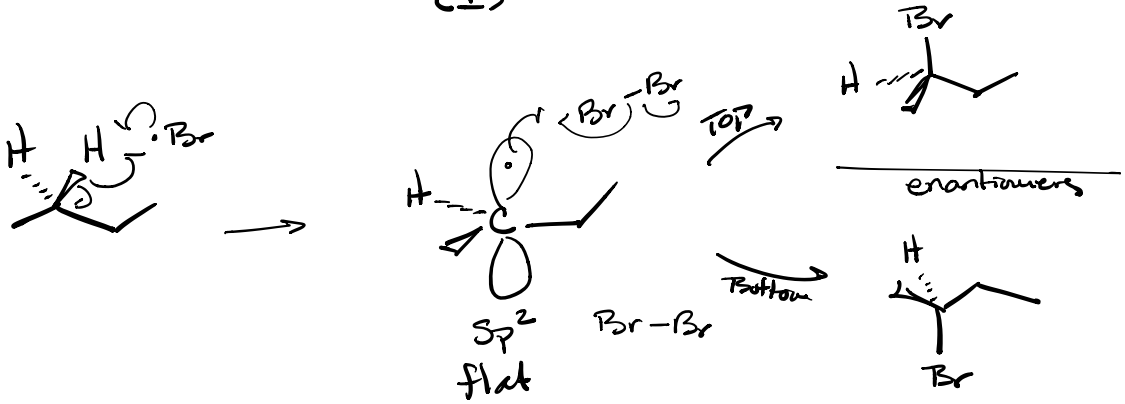
K_{rel} = Relative Rates

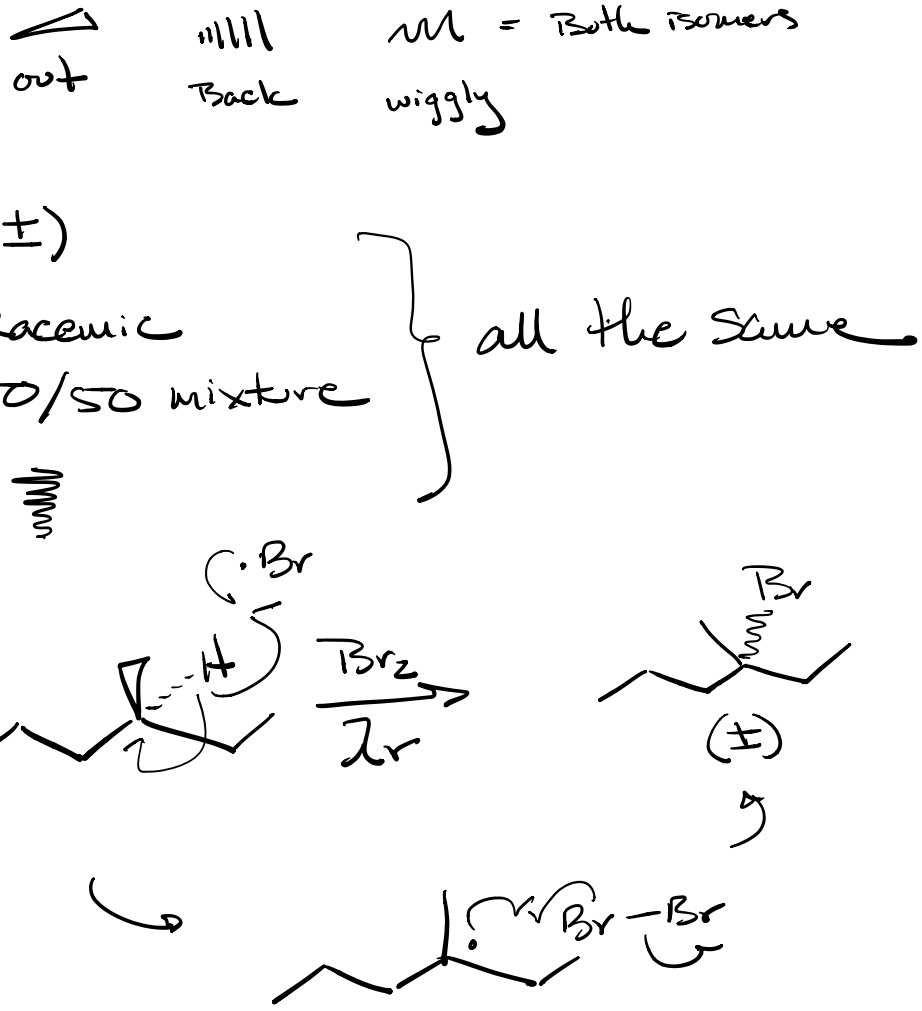
1°	2°	3°
1	82	1640



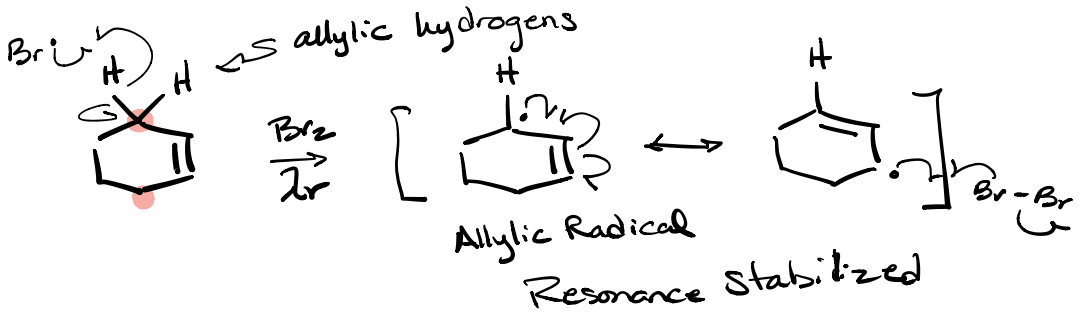
Stereochemistry

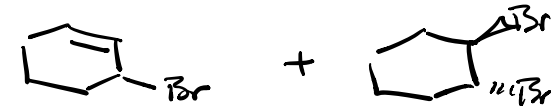


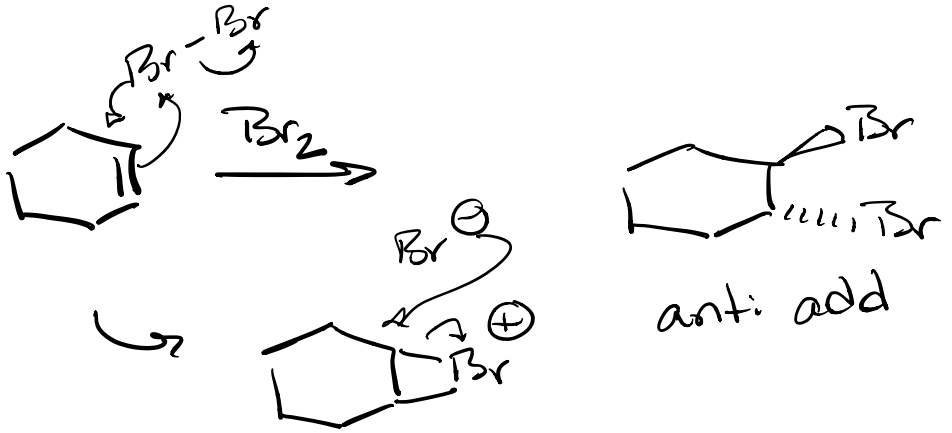



out
Back
= Both isomers
wiggly
(±)
Racemic
50/50 mixture
all the same
Br
H
Br2
hv
Br
(±)
Br
Br

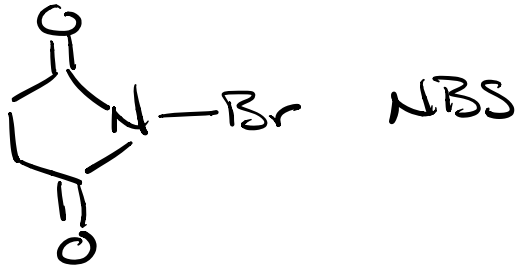
Allylic Halogenation

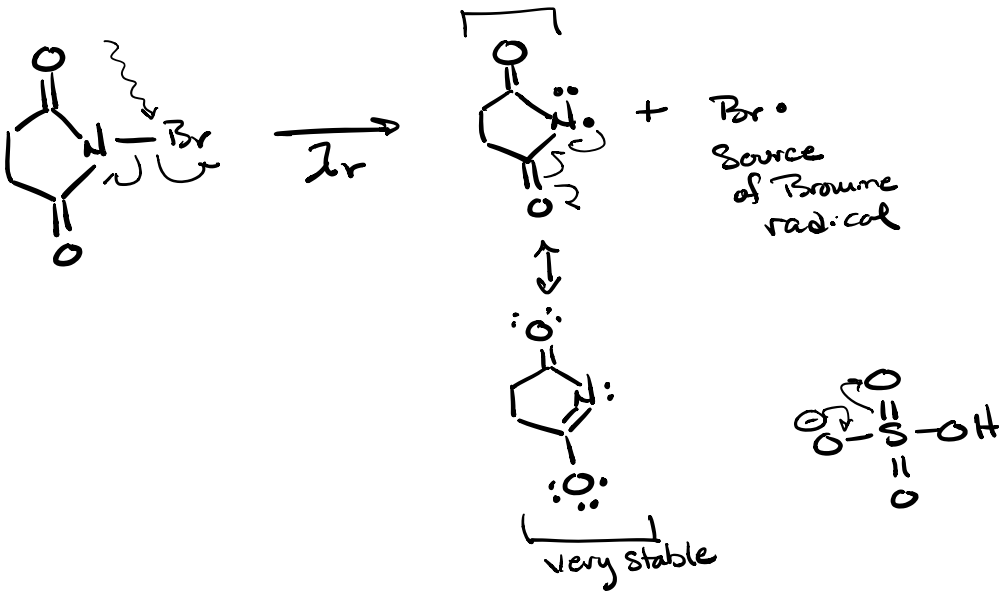


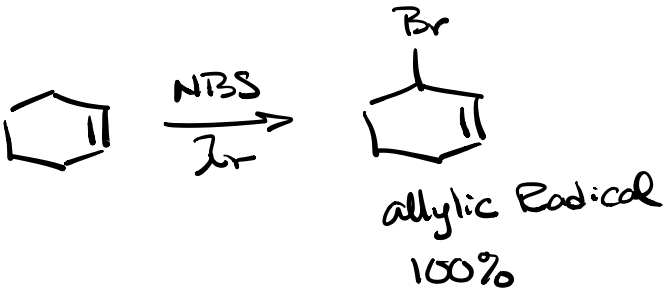


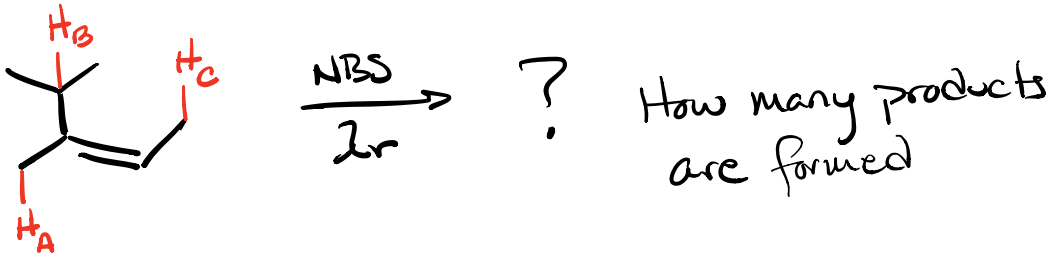


To avoid the electrophilic addition we use N-BromoSuccinimide

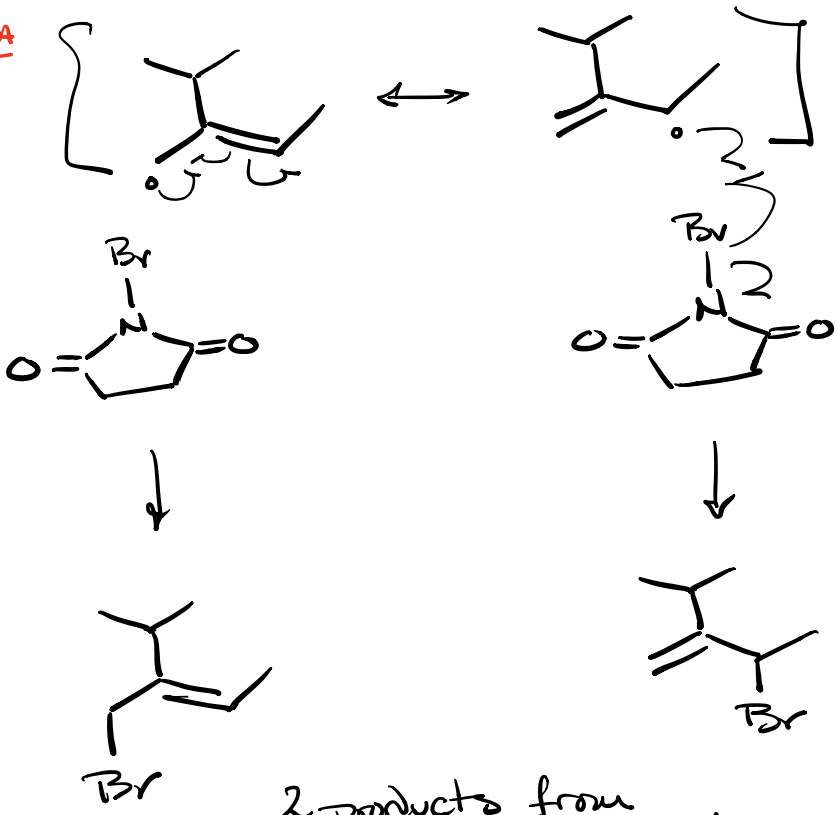



Br
hν
+
Br•
Source of Bromine radical
very stable

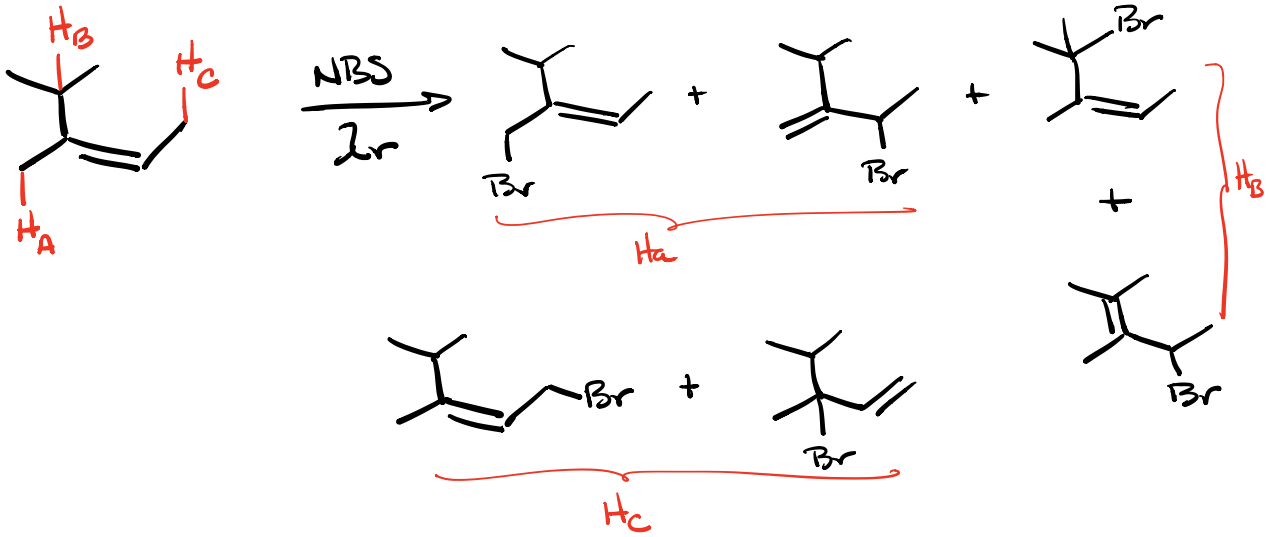

NBS
hν
Br
allylic Radical
100%

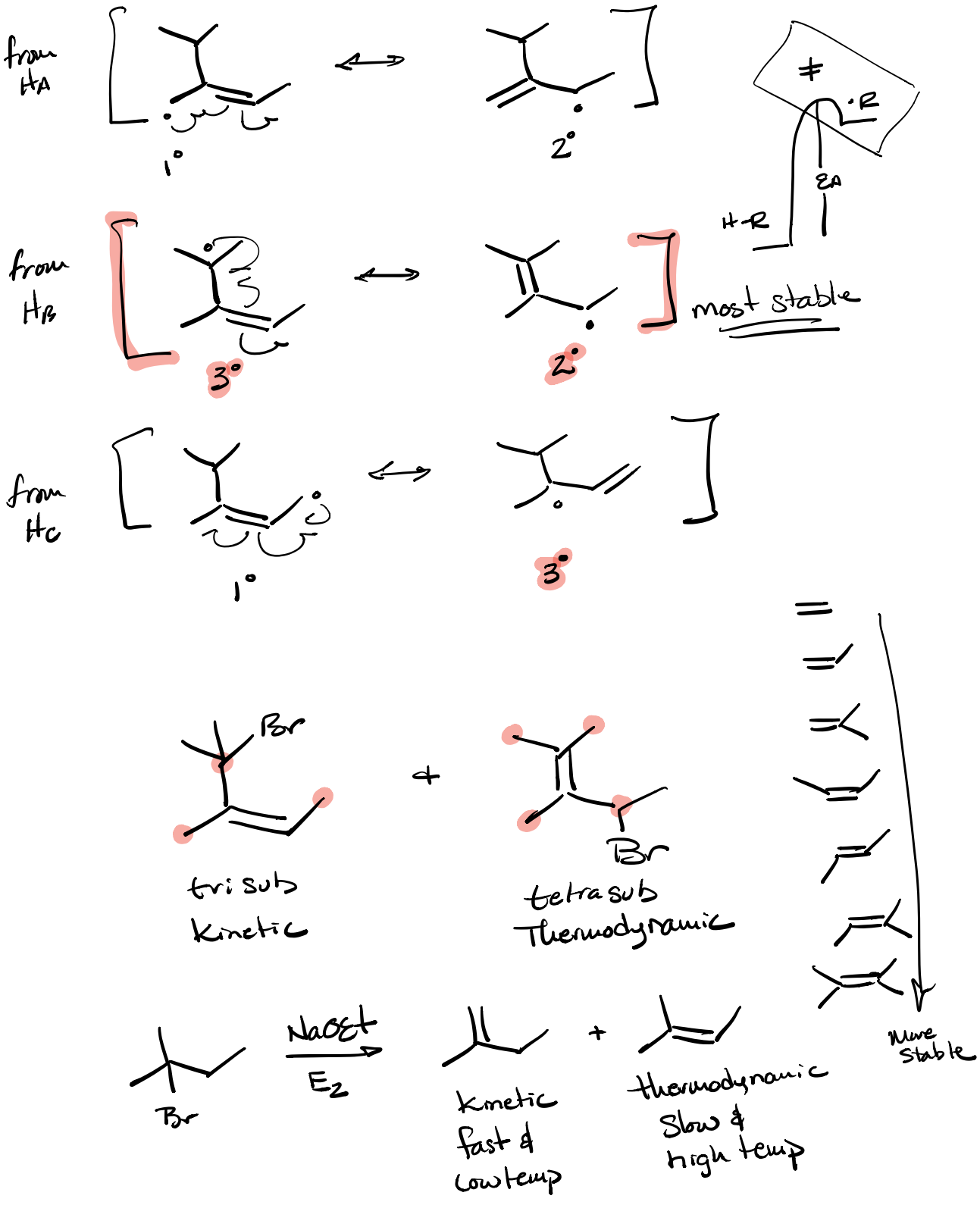

H_B
H_C
H_A
NBS
hν
?
How many products are formed

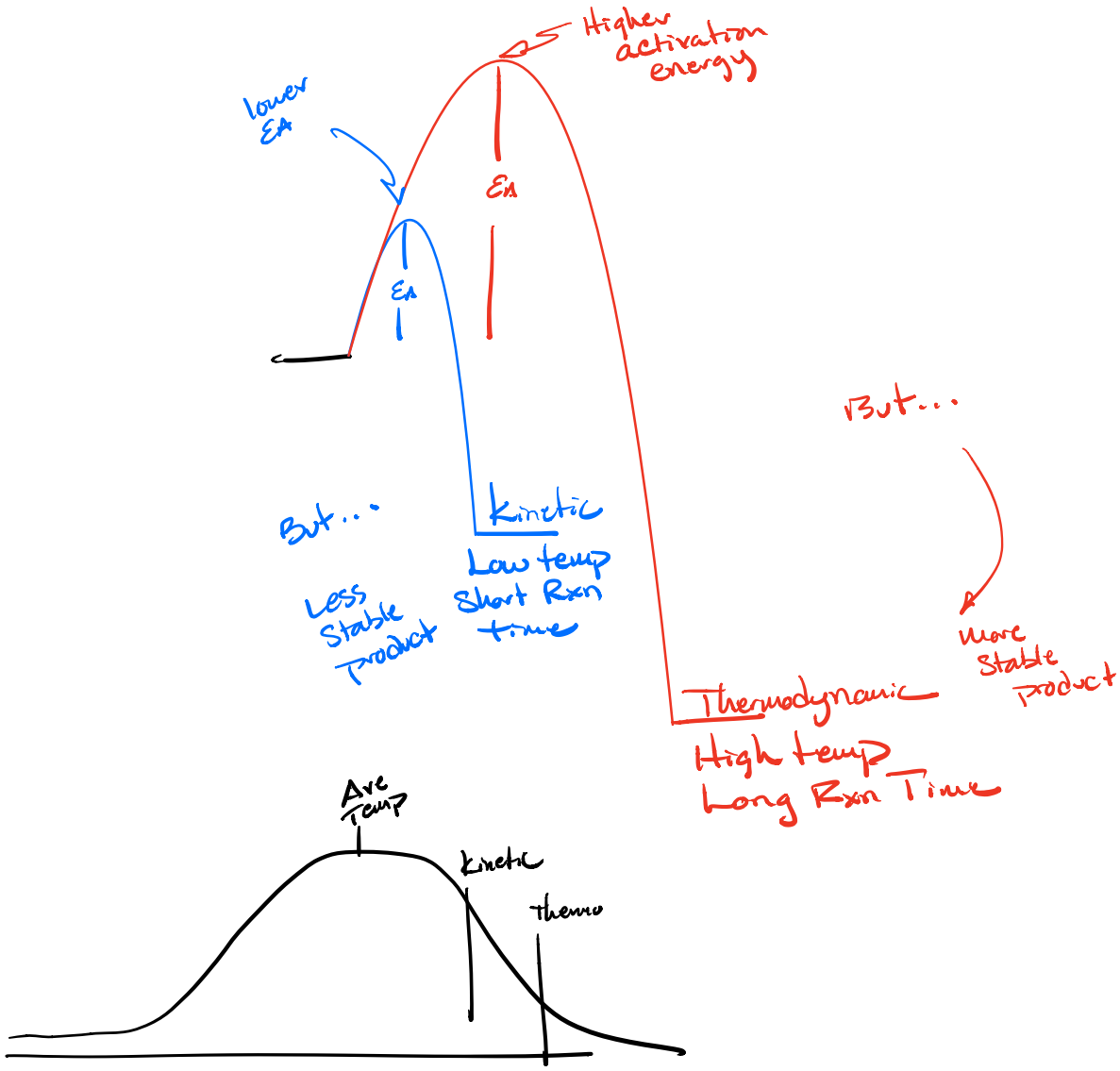
Pull H_A

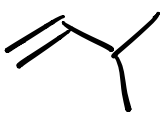


2 products from each allylic Radical

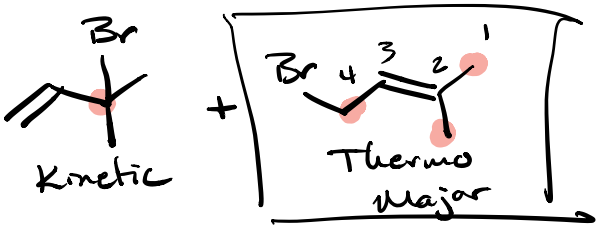


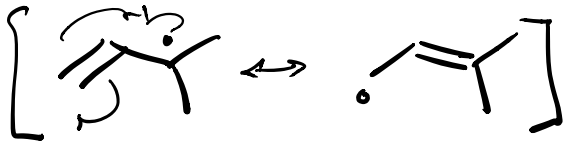

from HA
1°
2°
≠
·R
EA
H-R
from Hβ
3°
2°
most stable
from Hc
1°
3°
Br
tri sub
Kinetic
+
Br
tetra sub
Thermodynamic
more stable
Br
NaOEt
E2
Kinetic
fast &
Low temp
+
Thermodynamic
Slow &
high temp


Higher activation energy
lower Ea
Ea
Ea
But...
Kinetic
Low temp
Short Rxn time
Less Stable product
But...
more Stable product
Thermodynamic
High temp
Long Rxn Time
Ave Temp
Kinetic
Thermo



NBS
hv
CCl_4
60°C
(hot)
10 hrs
Hot & long
Run time

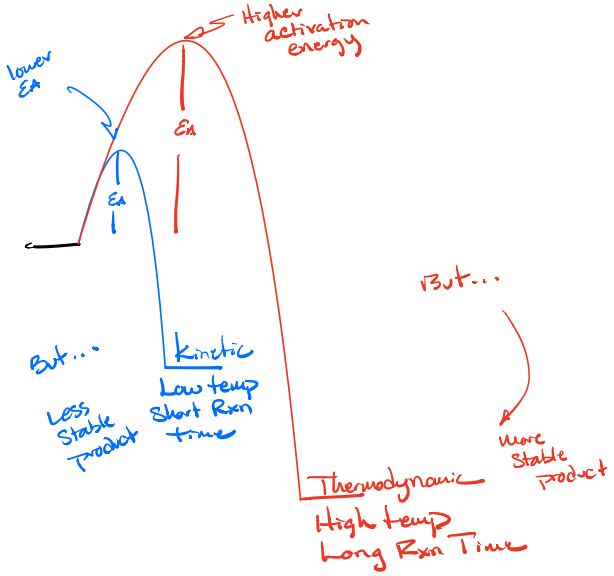




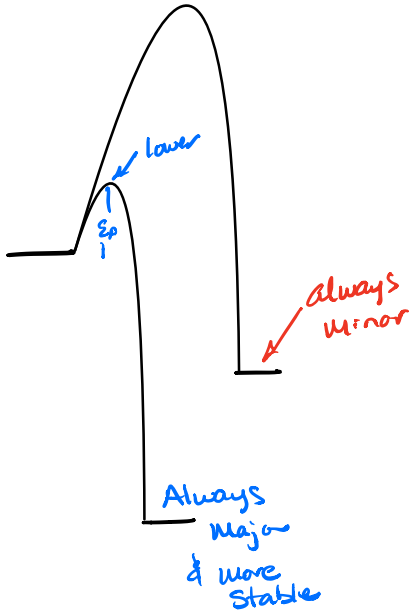
① pull allylic H
② Resonance
③ Substitute
④ draw products
⑤ assess double bonds
⑥ determin major for given conditions

4-Bromo-1-methyl-2-butene
or but-2-ene

Kinetic vs. Thermodynamic

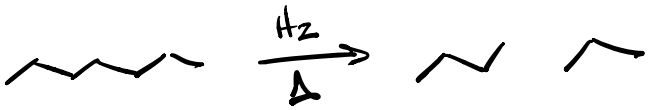


More Common



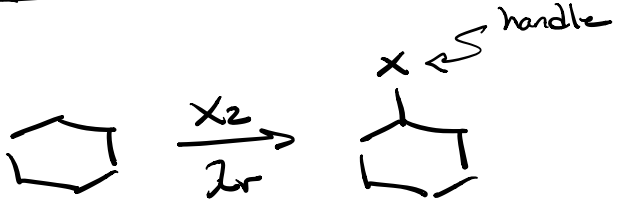
Hydrocarbon Processing (All thermo free radical)

Cracking 

hydrocracking 

Reforming 

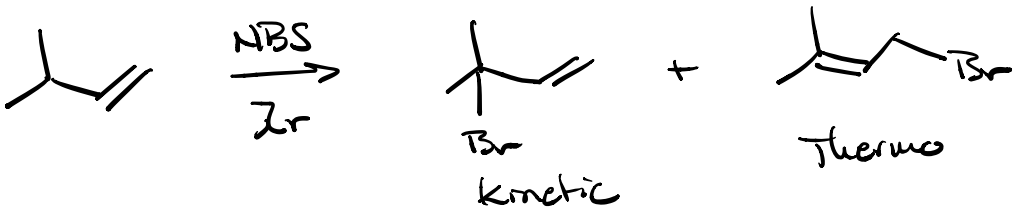
Synthetic Utility

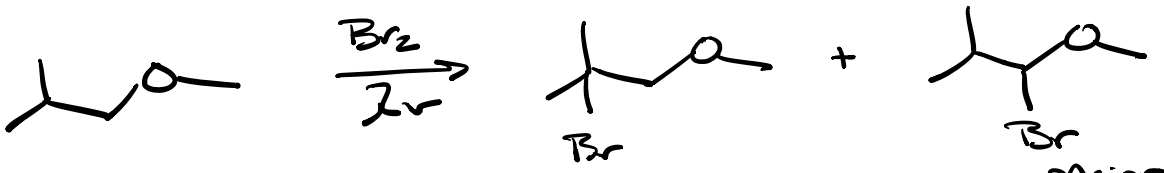


unfunctional → new functionality

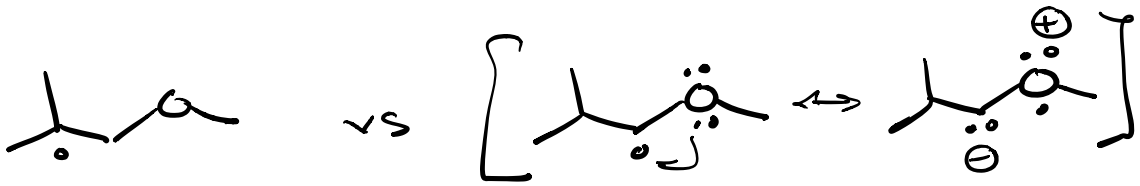
$3^\circ >> 2^\circ > 1^\circ$ for Br

But ....





which is major?

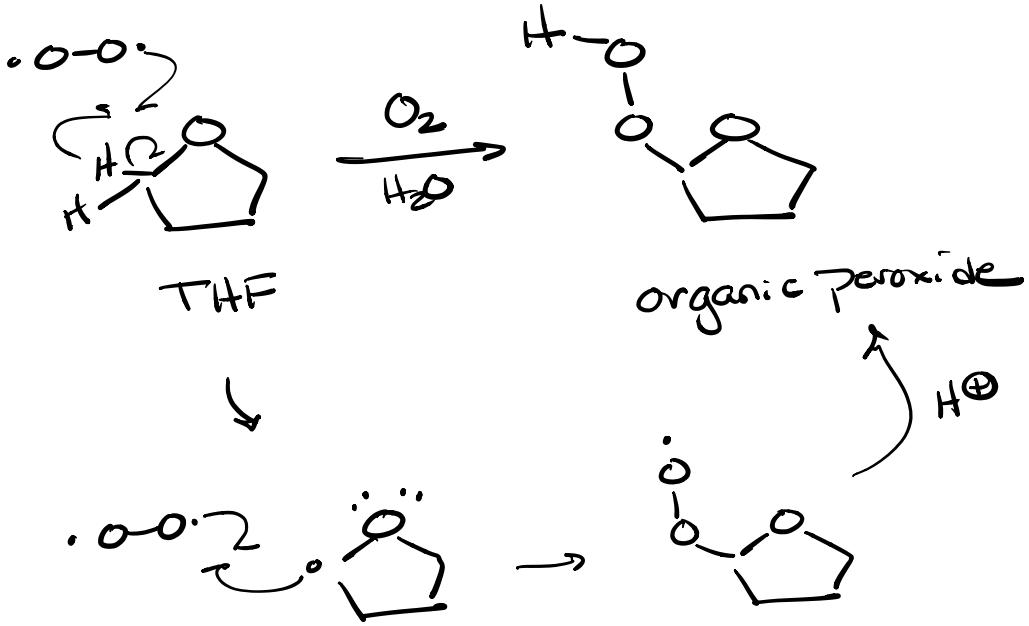


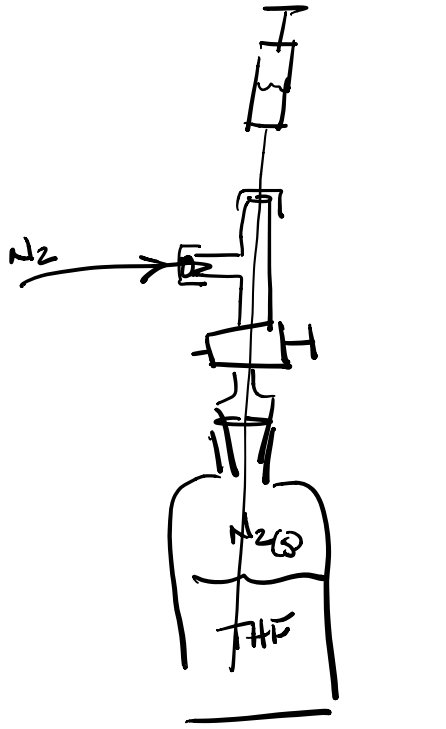
no Resonance

Resonance

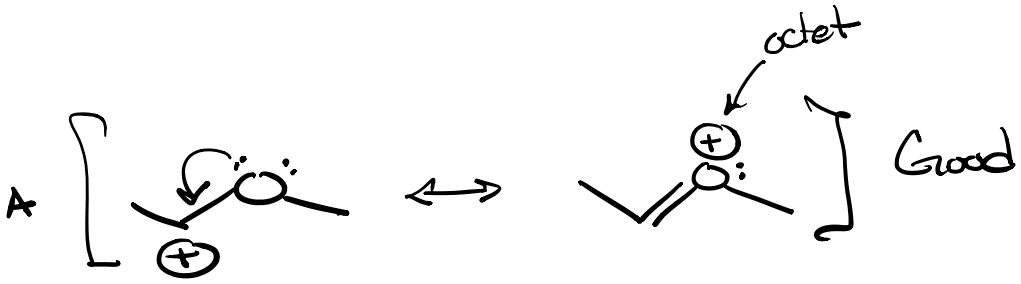
lower E_A

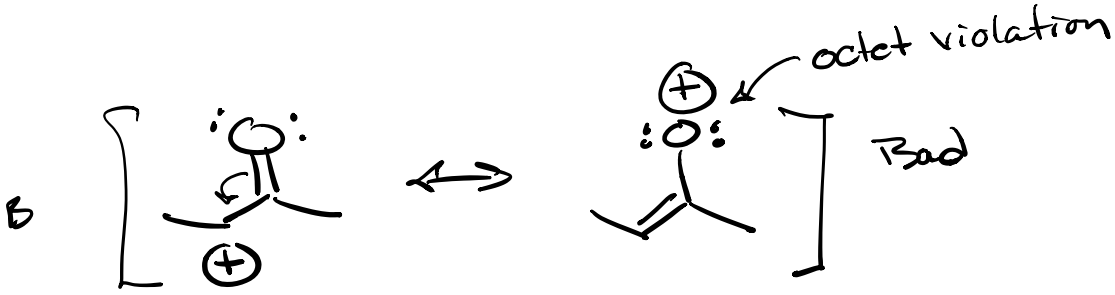
faster Rxn

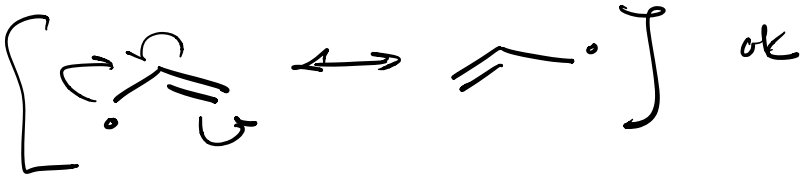

O2
H2O
THF
organic peroxide
H⊕

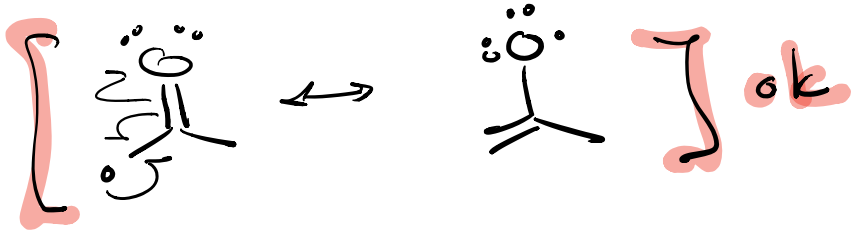

N2
N2(g)
THF

Resonance Stabilizing Groups

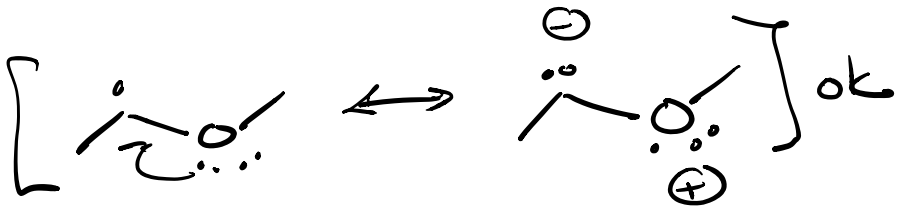


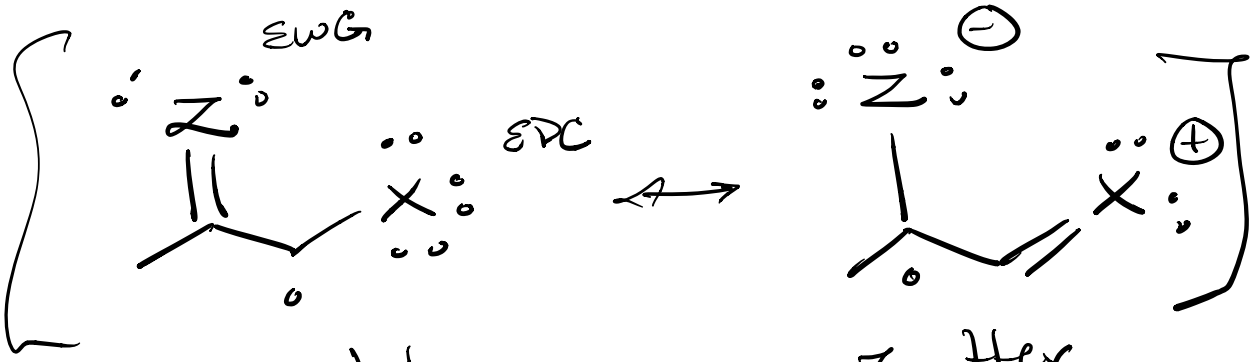






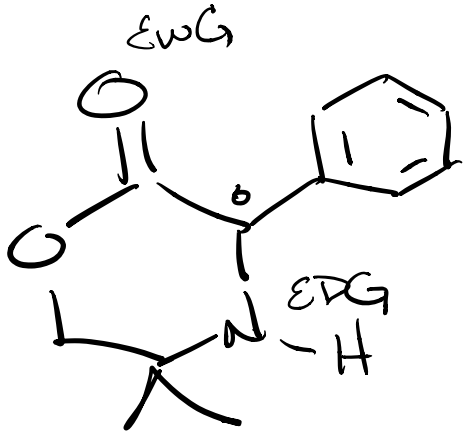
Free Radicals Stabilized by both EWG & EDG !



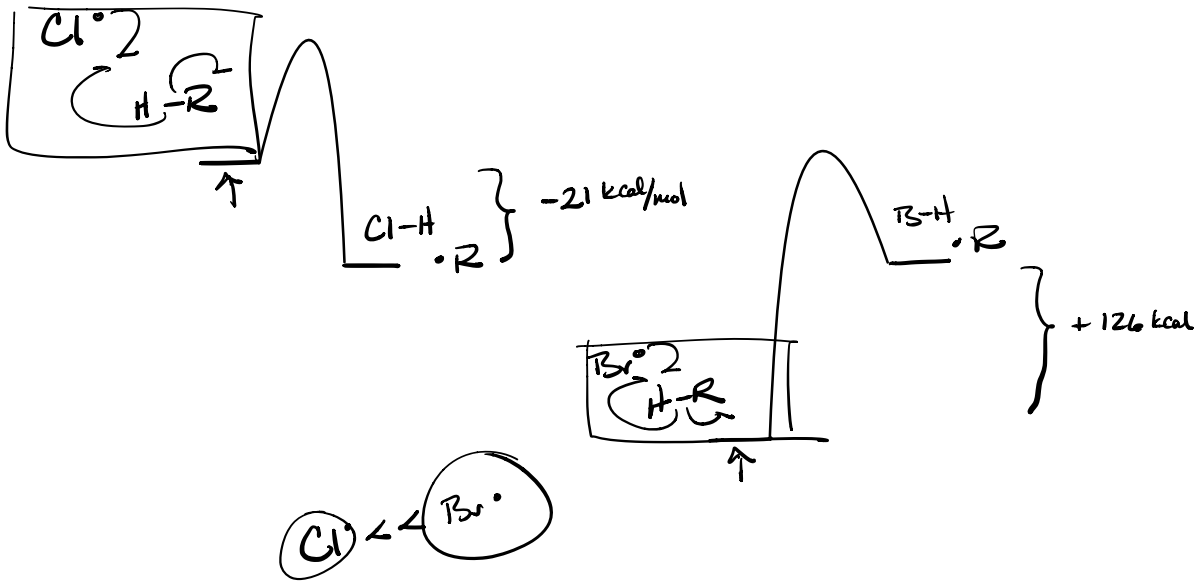


Captodative System Super Stable

Zwitter ion



stable at room temp for days


Cl· 2
H–R
Cl–H
·R
-21 kcal/mol
Br–H
·R
+ 126 kcal
Br· 2
H–R
Cl·
Br·